

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
1 March 2001 (01.03.2001)

PCT

(10) International Publication Number
WO 01/14452 A1

(51) International Patent Classification⁷: C08G 63/86,
63/82, 63/78

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(21) International Application Number: PCT/US99/19385

(22) International Filing Date: 24 August 1999 (24.08.1999)

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(25) Filing Language: English

(26) Publication Language: English

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MX, RU, US.

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(84) Designated States (*regional*): European patent (AT, BE,
CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC,
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Published:

— With international search report.

*For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.*

(54) Title: PREPARATION OF POLYESTERS EMPLOYING ANTIMONY CATALYSTS AND ACIDIC PHOSPHORUS COM-
POUNDS

(57) Abstract: The process for the production of polyesters, and in particular polyethylene terephthalate (PET) involves polymer-
ization, e.g., polycondensation, of one or more diacids and one or more diols in the presence of both an antimony catalyst and an
acidic phosphorus-containing additive like e.g. phosphoric acid. The acidic phosphorus additive is introduced prior to the antimony
catalyst, preferably by an amount of time to allow a reaction between the additive and at least one diol of the (s) present in the reaction
mixture. A polyester resin produced by this process is also provided.

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PREPARATION OF POLYESTERS EMPLOYING ANTIMONY CATALYSTS AND ACIDIC
PHOSPHORUS COMPOUNDS

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RELATED APPLICATION

This application is related to International Application [Needle & Rosenberg
Docket No. 05015.0233/P] filed concurrently herewith, which is incorporated herein
10 by reference in its entirety.

FIELD OF THE INVENTION

The present invention relates to processes for producing polyester resins and in
15 particular poly(ethylene) terephthalate (PET) containing low levels of phosphorus
containing additives that is suitable for use in a variety of applications including the
manufacture of articles such as containers.

BACKGROUND OF THE INVENTION

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It is well known in the art that polyesters such as poly(ethylene terephthalate)
(PET) are useful for many packaging applications. In fact, PET or modified PET is a
polymer of choice for making beverage and food containers, particularly carbonated
beverage containers.

25

Poly(ethylene terephthalate) may be derived from multistep processes well
known in the art which may include the direct esterification of ethylene glycol and
terephthalic acid. In addition, it is known that PET can be modified with additional
acidic and/or glycol comonomers, e.g., isophthalic acid (or dimethyl isophthalate),
30 1,4-cyclohexanedimethanol (CHDM), and the like. Modifying PET with additional
comonomers may improve some of the physical properties of the resulting polyesters

and provide particularly desired properties in an article formed from the polyester particularly in the areas of crystallization and processability.

5 Polyesters such as PET are typically formed via three-stage processes. The three preferred stages are often referred to as the esterification stage, the prepolymer stage, and the polycondensation stage.

10 Each of the stages can employ catalysts and certain additives. For example, since both the prepolymer stage and the polycondensation stage employ the same basic reaction, a variety of polycondensation catalyst systems are recognized in connection with the prepolymer and polycondensation stages. Examples of such catalysts includes titanium, gallium, germanium, tin, and antimony compounds. The use of additives is also known in the art. Additives that are recognized in the art include phosphorus-containing stabilizers such as phosphates and phosphoric acid. In 15 this regard, such phosphorus-containing additives are considered interchangeable.

As background in this regard, attention is directed towards the following patents that discuss the use of phosphorus-containing additives:

20 U.S. Patent 4,499,226, issued Feb. 12, 1985, and assigned to Goodyear Tire & Rubber Company, discloses process for producing high clarity colorless polyesters which include the use of polycondensation catalysts, cobalt-containing compounds and phosphorus-containing additives.

25 German Patent Application 195 37 930 A1, opened to public inspection on April 17, 1997, and assigned to Zimmer, AG, also discloses a continuous process for the production of transparent polyesters in which unpurified diol that has been eliminated during the polycondensation stage can be internally recycled into the process.

30

U.S. Patent 4,110,316, issued Aug. 29, 1978 and assigned to E.I. Du Pont de Nemours and Company, discloses a process for producing fiber-forming polyester from ethylene glycol and terephthalic acid that includes the use of color inhibitors such as phosphoric acid and triphenyl phosphite.

5

U.S. Patent 5,243,022, issued Sept. 7, 1993 and assigned to Korea Institute of Science and Technology, discloses a method for forming polyesters that involves forming prepolymers from a first portion of esterification product in the presence of certain catalysts and stabilizers. The prepolymers are then polycondensed together
10 with a second portion of esterification product to form the polyester.

U.S. Patent 5,235,027, issued Aug. 10, 1993 and assigned to Zimmer Aktiengesellschaft, discloses a process for making a modified copolyethylene terephthalate that includes the addition of a phosphorus-oxygen compound before
15 polycondensation in an amount that corresponds to a Sb: P weight ratio of at least four.

However, careful consideration of the art reveals serious errors, inconsistencies and contradictions in the way the art views phosphorus-containing
20 additives, particularly the use of low levels of acidic additives in polyester formation.

SUMMARY OF THE INVENTION

The present invention is based, in part, on the surprising discovery that the
5 choice of phosphorus-containing additive, when employed in connection with certain
polymerization catalysts, can have a significant impact on reaction rate of the
polymerization process as well as the clarity of the resulting polyester. Further, it was
surprisingly found that the optimal relative addition sequence of the catalyst and
phosphorus-containing additive was impacted by the both choice and level of
10 phosphorus-containing additive.

One aspect of the present invention involves a process for making a polyester
resin including the steps of:

- (a) esterifying at least one dicarboxylic acid component and at least one
15 diol component; and
- (b) polymerizing the product of step (a) under conditions effective to
provide a polyester resin,

wherein the polymerization step (b) occurs in the presence of (i) an antimony-based
polymerization catalyst and (ii) an acidic phosphorus-containing additive, with the
20 additive (ii) being added prior to the catalyst (i) so as to provide a polyester resin that
is at least substantially free of inorganic compounds formed from a reaction of the
catalyst (i) and additive (ii). The amount of additive is preferably not greater than
about 45 ppm based on elemental phosphorus in the resulting polyester.

25 In addition the process can include a prepolymer stage between steps (a) and
(b). The process can further include additional step such as solid-phase
polymerization of the polyester resin from step (b). Moreover, the polymerization step
(b) is preferably performed in the absence of added cobalt compound(s).

Another aspect of the present invention relates to a process that includes (a) esterifying at least one dicarboxylic acid component and at least one diol component; and

polymerizing the product of step (a) under conditions effective to provide a polyester resin, wherein the polymerization step (b) occurs in the presence of (i) an antimony-based polymerization catalyst and (ii) an acidic phosphorus-containing additive, with the catalyst (i) being added after, the additive (ii), and the acidic phosphorus containing additive (ii) is added sufficiently before the polycondensation catalyst (i) such that the additive (ii) can react with the at least one diol.

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Yet another aspect of the present invention include process for making polyester resin that includes (a) esterifying at least one dicarboxylic acid component and at least one diol component; and (b) polymerizing the product of step (a) under conditions effective to provide a polyester resin, wherein the polymerization step (b) occurs in the presence of (i) an antimony-based polymerization catalyst and (ii) an acidic phosphorus-containing additive, with the catalyst (i) being added after, the additive (ii), because of the order of additive employed in the present invention, the reaction rate of the polymerization step (b) is relatively insensitive to the level of additive (ii).

20

In another aspect, the present invention relates to a polyester, and in particular, a poly(ethylene terephthalate) (PET) resin or a modified PET resin which is preferably made by the inventive process. In this regard, the polyester contains elemental phosphorus in an amount not greater than 45 ppm and organic toners in an amount of about 0.5 to about 10 ppm. Moreover, polymer resulting from step (b) is preferably at least substantially free of antimony phosphate compounds. The polyester resin preferably has an intrinsic viscosity of about 0.4 to 1.2 dL/g measured at 25 C by dissolving 250 mg of polyester in 50 mL of a solvent consisting of a 60:40 ratio by weight of phenol and 1,1,2,2-tetrachloroethane.

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BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 illustrates the effect on phosphorus level on DEG level of the esterification product when phosphoric acid is added before esterification stage;

5

Fig. 2 illustrates the effect on reaction rate, as represented by time in the polycondensation stage, of changing phosphorus and antimony levels when acidic phosphorus-containing compounds are introduced prior to the antimony catalyst;

10

Fig. 3 illustrates the effect on reaction rate, as represented by time in the polycondensation stage, of changing phosphorus and antimony levels when acidic phosphorus-containing compounds are introduced after the antimony catalyst.

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DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention relates to a process for making polyester resins and in particular, poly(ethylene terephthalate), which employs the use of acidic phosphorus-containing additives. The amount, and point of introduction, for the acidic phosphorus-containing additives can be optimized so as to provide for an improved process, e.g., a decreased reaction time, and a desired product, e.g., a polyester having improved clarity.

In one preferred aspect, it has been surprisingly discovered that acidic phosphorus-containing additives such as phosphoric acid, do not react in the same manner as non-acidic phosphorus-containing compounds, such as phosphate triesters. In fact, they can have very different, effects on the polymerization stage. For example, it has been discovered that where acidic phosphorus-containing compounds are introduced prior to certain polymerization catalysts, one can provide for relatively high reaction rates at certain phosphorus levels.

30

It was also surprisingly found that the process of the present invention can provide for the reduction, and possibly even elimination, of antimony phosphate crystals in the resulting polyester. This ability to reduce the amount, size or both of antimony phosphate crystals can effectively reduce the particulate haze in the polyester.

With the foregoing in mind, the polyesters may be prepared in accordance with techniques that are recognized in the art. To this end, polyesters are any crystallizable polyester homopolymer or copolymer, preferably those polyesters suitable for use in packaging, and particularly food packaging.

Suitable polyesters are generally known in the art and may be formed from aromatic dicarboxylic acids, esters of dicarboxylic acids, anhydrides of dicarboxylic esters, glycols, and mixtures thereof. More preferably the polyesters are formed from diacids such as terephthalic acid, isophthalic acid, and 2,6-naphthalenedicarboxylic acid, and mixtures thereof, and diols such as ethylene glycol, diethylene glycol, 1,4-cyclohexane dimethanol, 1,4-butanediol, and mixtures thereof.

As discussed above the process of the present invention can produce the polyesters and "modified" polyesters. By "modified" it is meant that the preferred diacids and/or diols are substituted with one or more diacid or diol components. For example, the preferred diol, e.g., ethylene glycol in the case of PET, is substituted with one or more diols and/or the preferred acid component, e.g., terephthalic acid, in the case of PET, is substituted with one or more acid components.

25

Specifically, the dicarboxylic acid component of the polyester may optionally be substituted with up to about 20 mole percent of one or more different dicarboxylic acids. Such additional dicarboxylic acids include aromatic dicarboxylic acids preferably having 8 to 14 carbon atoms, aliphatic dicarboxylic acids preferably having 4 to 12 carbon atoms, or cycloaliphatic dicarboxylic acids preferably having 8 to 12 carbon atoms. Examples of dicarboxylic acids to be included with terephthalic acid

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are: phthalic acid, isophthalic acid, naphthalene-2,6-dicarboxylic acid, 1,4-cyclohexanedicarboxylic acid, 1,3-cyclohexanedi-carboxylic acid, stilbene dicarboxylic acid, cyclohexanedi-acetic acid, 1,12-dodecanedioic acid, diphenyl-4, 4'-dicarboxylic acid, succinic acid, glutaric acid, adipic acid, azelaic acid, sebacic acid, mixtures thereof and the like.

In addition, the glycol component may optionally be substituted with up to about 20 mole percent, of one or more different diols other than ethylene glycol. Such additional diols include cycloaliphatic diols preferably having 6 to 20 carbon atoms or aliphatic diols preferably having 3 to 20 carbon atoms. Examples of such diols include: diethylene glycol, triethylene glycol, 1,4-cyclohexanedimethanol, propane-1,2-diol, propane-1,3-diol, butane-1,4-diol, pentane-1,5-diol, hexane-1,6-diol, 3-methylpentanediol-(2,4), 2-methylpentanediol-(1,4), 2,2,4-trimethylpentane-diol-(1,3), 2-ethylhexanediol-(1,3), 2,2-diethylpropane-diol-(1,3), hexanediol-(1,3), 1,4-di-(hydroxyethoxy)-benzene, 2,2-bis-(4-hydroxycyclohexyl)-propane, 2,4-dihydroxy-1,1,3,3-tetramethyl-cyclobutane, 2,2-bis-(3-hydroxyethoxyphenyl)-propane, 2,2-bis-(4-hydroxypropoxyphenyl)-propane, 1,2-cyclohexane diol, 1,4-cyclohexanediol, mixtures thereof and the like. Polyesters may be prepared from two or more of the above diols. Moreover, the foregoing diols may be in their cis- form, trans- form or mixtures thereof.

The process of the present invention can employ art-recognized steps or stages in forming polyesters. In the context of the present invention, the preferred stages are:

- (1) an esterification stage, including but not necessarily limited to direct esterification; and
- (2) a polymerization stage, including but not limited to a polycondensation reaction.

Moreover, a prepolymer stage also including but not limited to polycondensation, is preferably performed between the esterification and polymerization stages.

Although the singular may be used in connection with the various stages, each of stages may include one or more steps or substages. For example, the esterification and/or prepolymer stages may each include one or more reaction steps or substages having differing reaction conditions, e.g., progressively lower pressures and
5 temperature. Finally, although these stages are generally recognized in the art, preferred conditions are set out below for convenience and clarity.

In this regard, the esterification stage typically involves heating a mixture of one or more dicarboxylic acids, preferably aromatic dicarboxylic acids, and one or
10 more diols under suitable conditions and in the optional presence of esterification catalysts. Examples of such conditions include temperatures in the range of about 200°C to about 300°C, preferably 240°C to about 280°C, and pressures of about 0 to about 100, preferably about 0 to about 50 psig. The optional esterification catalysts can be used alone or in combination. When used the total amount of catalyst is less
15 than about 200 ppm, more preferably less than 100 ppm, on an elemental basis in the resulting polymer. It is more preferred that no catalyst be employed. Suitable colorants may also be added at this point to control the final color of the polyester. The reaction is typically conducted for about 1 to about 4 hours. It should be understood that generally the lower the reaction temperature, the longer the reaction
20 will have to be conducted.

The esterification stage typically produces a monomer and oligomer mixture continuously in a series of one or more reactors. Alternately, the monomer and oligomer mixture could be produced in one or more batch reactors.

25

In a prepolymer stage, the mixture of polyester monomer and oligomers undergoes a suitable polymerization step, typically melt-phase polycondensation, to produce a low molecular weight precursor polymer. The precursor polymer is produced in a series of one or more reactors operating at elevated temperatures. This
30 can involve the a single stage, or one or more substages. To this end, the prepolymer stage can involve the use of one or more reactors operated continuously, one or more

batch reactors or even one or more reaction steps or substages performed in a single reactor vessel.

The precise reaction conditions are dependent upon the nature of the reactants and the final product. However, to facilitate removal of excess glycols, water, alcohols, aldehydes, and other reaction products, the reactors are typically run under a vacuum or purged with an inert gas. Inert gas is any gas which does not cause unwanted reaction or product characteristics at reaction conditions. Suitable gases include, but are not limited to CO₂, argon, helium and nitrogen. The prepolymer stage is typically conducted at a temperature less than about 300°C, and preferably between about 240°C and about 290°C at a pressure sufficient to aid in removing reaction products such as ethylene glycol.

The next stage, which is the polymerization stage, also typically involves the melt-phase polycondensation of the prepolymer product. Although the polymerization stage typically involves the same basic chemistry as the prepolymer stage, the fact that the size of the molecules, and thus the viscosity differs, means that the reaction conditions also differ. A wide variety of reaction conditions, are employed in the art, and as such they all will not be described here. However, the present invention contemplates the use of the wide range of polymerization options that are recognized in the art as being suitable for use with polyesters.

The primary requirement for the polymerization stage according to the present invention is that it be performed in the presence of both a suitable catalyst and a phosphorus additive. In the context of this invention, the additive is introduced prior to the catalyst. While the exact point of introduction for the additive is not critical as long as the additive can suitably react with the diol(s) prior to introduction of the catalyst. According to the present invention, catalyst is added any point after the additive

In some embodiments, it is preferred that the additive be introduced, during, the esterification stage, or prior to or during a prepolymer stage. It is also preferred that the catalyst be introduced at any point after the additive and preferably, immediately prior to, or during, the prepolymer stage as long as it is introduced before
5 the polymerization stage and sufficiently after the additive to allow the additive to react with the diol(s). Where more than one reaction step or sub-stage is employed in the prepolymer stage, it is more preferred to have the phosphorus introduced in a substage prior to the substage when the catalyst is added.

10 Where the additive is introduced prior to or during the esterification stage, the amount of DEG can be controlled. That is, the later the additive is introduced the less DEG would be expected to be produced. Steps could be taken to reduce the level of DEG formed. The addition point of the acidic phosphorus-containing additive may be optimized to reduce DEG formation. The rate of diethylene glycol formation is
15 mainly proportional to the concentration of ethylene glycol (EG) end groups. As esterification progresses, the DEG will increase, and there will be fewer EG end groups. Adding the acidic phosphorus-containing compound later in the process may minimize DEG formation. Moreover, there are a variety of art-recognized techniques for reducing the DEG concentration including that discussed in U.S. Patent No.
20 5,252,513, which is incorporated by reference in its entirety.

In addition, where the phosphorus additive is added during esterification, it is preferred that the additive be introduced late in the stage, preferably after 90%, more preferably after 95% and still more preferably after 98% conversion in the selected
25 stage.

As examples of suitable addition sequences where more than one esterification sub-stage is employed, phosphoric acid may be added between the first and second esterification stage while the antimony is added after the second esterification stage
30 and before the first prepolymer stage. Further, phosphoric acid may be added after the

last esterification stage and before the first prepolymer stage while the antimony is added during the prepolymer stage.

Where more than one reaction step or sub-stage is employed in the prepolymer stage, it is more preferred to have the catalyst introduced prior to the final reaction step a sub-stage in order to provide optimal mixing time prior to the polymerization step.

The preferred polymerization catalyst for use in the process of the present invention is an antimony-based polymerization catalyst. Suitable antimony based catalyst include antimony (III) and antimony (V) compounds recognized in the art and in particular, diol-soluble antimony (III) and antimony (V) compounds. Other suitable compounds include those antimony compounds that react with, but are not necessarily soluble in, the diols, with examples of such compounds including antimony (III) oxide.

Specific examples of suitable antimony catalysts include antimony (III) oxide and antimony (III) acetate, antimony (III) glycolates, antimony (III) ethyleneglycoxide and mixtures thereof, with antimony (III) oxide being preferred.

The preferred amount of catalyst added is that effective to provide an elemental antimony level of between about 75 and about 400 ppm by weight of the resulting polyester.

The phosphorus-containing additive employed in the present invention can be any acidic phosphorus-containing compound recognized in the art. Suitable examples of such additives include phosphoric acid, phosphorous acid, polyphosphoric acid, acidic phosphite esters, acidic phosphate esters such as phosphate mono- and di-esters, and mixtures thereof, among others.

The acidic phosphorus-containing additive is present in an amount effective to provide a desired reaction rate. When a desired amount of acidic phosphorus-containing additive is added prior to the antimony catalyst, the polymerization rate can be largely insensitive to phosphorus level and can even be optimized for certain phosphorus levels. For example, it was found for antimony catalyst corresponding to
5 elemental antimony levels on the order of 210 ppm, and the phosphorus levels were about 20-25 ppm, reaction rates were comparable or better than reaction rates after the reverse addition order.

10 The acidic phosphorus-containing additive can also be present in an amount effective to provide a polyester resin that is at least substantially free of inorganic compounds that are reaction products of the catalyst and the additive and can cause haze in the polyester. That is, under certain conditions, a polycondensation catalyst(s) and an acidic phosphorus-containing additive(s) can react with each other to produce
15 certain inorganic compounds, such as antimony phosphate. Such inorganic compounds can cause particulate haze in polyesters.

When acidic phosphorus-containing compounds are added prior to the catalyst in the manner of the present invention, the formation of such inorganic compounds
20 can also be reduced or even eliminated. When a polycondensation process minimizes the formation of such inorganic compounds, the process is more likely to produce polyesters without undesirable levels of particulate haze, which precludes clarity. Accordingly, the process of the present invention is capable of producing a polyester resin "at least substantially free" of such inorganic compounds, and in particular, at
25 least substantially free of antimony phosphates.

By "at least substantially free," it is meant that the polyester resin does not include levels of the above-discussed inorganic compounds such as antimony phosphates; that create a particulate haze which can have a negative visual impact
30 upon the resin melt or articles formed from the resin.

The preferred amount of acidic phosphorus-containing additive is that effective to provide a relatively low elemental phosphorus level, i.e., not greater than about 75 ppm based on the weight of the polyester. Suitable levels fall both in the “high” end of that range, e.g., about 45 to about 75 ppm, “mid” levels of 20-45 ppm, and “low” end, of the range, e.g., less than about 15 ppm. Although the chemistry does not impose a lower limit, the amount is typically not less than 1 ppm. The foregoing amounts are by weight of elemental phosphorus in the resulting polyester.

The phosphorus-containing additive is preferably introduced in a solution of the diol(s). To this end, any concentration that is capably providing the desired phosphorus level can be employed. Suitable concentrations include those greater than about 1 % wt., preferably about 3 to about 15 % by weight of the additive in the diol.

Temperatures for the polymerization stage are generally between about 240°C to about 300°C and a pressure between about 0 and about 2 mm Hg. Once the desired inherent viscosity (I.V.) is reached, the polymer is pelletized. Precursor I.V. is generally below about 0.7 to maintain good color. The target I.V. is generally selected to balance good color and minimize the amount of solid stating which is required. Preferably, the I.V. of a polyester of this invention is from about 0.40 dl/g to about 1.2 dl/g. Inherent viscosity was measured at 25°C using 0.50 grams of polymer per 100 ml of a solvent consisting of 60% by weight phenol and 40% by weight tetrachloroethane.

The resulting polymer can then be subjected to further polymerization reaction, e.g., solid phase polymerization (also know as “solid-stating”) by techniques which are known in the art and as such are not described in detail here.

Also, although not required, additives normally used in polyesters may be used if desired. Such additives include, but are not limited to colorants, pigments, carbon black, glass fibers, fillers, impact modifiers, antioxidants, stabilizers, flame retardants, reheat aids, acetaldehyde reducing compounds and the like.

In addition, certain organic toners, e.g., blue and red organic toners, such as those described in U.S. Patents 5,372,864 and 5,384,377, which are incorporated by reference, can be used. As discussed in these U.S. Patents, specific examples of
5 suitable blue toners include substituted 1,4-bis(2,6-dialkylanilino) anthraquinones) while suitable red toners include anthraquinone and anthrapyridone (3-H-dibenz[f,i]isoquinoline-2,7-dione) compounds. The total amount of organic toners in the polymer is preferably 0.5 to about 10 ppm. To this end, about 0.5 to about 3 ppm of organic red toner(s) and about 1 to about 7 ppm of organic blue toner(s) are more
10 preferred.

The polyester is preferably devoid of any added cobalt compounds. That is, while certain very minor amounts of certain cobalt compounds may be present in the diacid(s) and/or diol(s) starting materials, no cobalt-containing compounds are added
15 during the process. Moreover, the polyester is preferably devoid of zinc, gallium, and silicon compounds.

While the resin may also contain small amounts of polyfunctional (comonomers, e.g., trifunctional or tetrafunctional comonomers such as trimellitic
20 anhydride, trimethylolpropane, pyromellitic dianhydride, pentaerythritol, and other polyester forming polyacids or polyols generally known in the art. The use of such polyfunctional comonomers is optional. That is, they may or may not be present.

The polyesters according to the present invention can be used in forming a
25 variety of articles including sheets, films, tubing, profiles, preforms, fibers, woven and shaped articles, such as containers, and thermoformed articles such as trays and the like.

The present invention will now be described in terms of the following example
30 which example are offered to illustrate the invention. The examples, however, in no way limit the scope of the invention.

EXAMPLES

A. Esterification Procedure

5 Terephthalic acid (TPA) was esterified with plant grade ethylene glycol (EG) and distilled cyclohexanedimethanol (CHDM), where the CHDM content of the copolyester was one and a half mole percent of the total glycols. The esterification was done in a continuous unit and was followed by batch-wise polycondensation. The
10 esterification was carried out in two continuous reactors connected in series (R1 and R2). A third vessel (R3) was used as a flash tank and for collection of the esterification product. The fixed volume reactors had approximately a 2:1 volume ratio with 2230 mL in R1 and 1100 mL in R2. The feed mole ratio of total glycols to terephthalic acid was 1.35. The amount of CHDM in the feed was 1.5 mole percent of
15 the terephthalic acid in the feed slurry, with the excess diol in the feed slurry being ethylene glycol. Slurry ingredients were mixed in a blender and added to a feed tank. The feed rate was 10 mL/min. The temperature target in R1 was 262 deg. C. The temperature target in R2 was 267 deg. C. The pressure targets for R1 and R2 were 36.5 PSIG and 18.5 PSIG, respectively. Substantially all the ethylene glycol vaporized
20 from R1 was condensed and returned directly to R1.

 In the esterification phase of the designed experiment, the factors being varied were additive type and level. The additive was mixed into the TPA/glycol slurry. For a summary of the additive or catalyst type and level target for each run, see the table
25 below.

Sample	Additive/catalyst	Level Target (ppm)	Phosphorus Source
1	None		
2	P	30	H ₃ PO ₄
3	P	50	H ₃ PO ₄
4	P	30	H ₃ PO ₄
5	P	10	H ₃ PO ₄
6	P	62	H ₃ PO ₄
7	P	30	H ₃ PO ₄
8	Sb	200	
9	Sb	250	
10	Sb	200	
11	Sb	150	
12	Sb	250	
18	Sb	150	
19	P	30	H ₃ PO ₄
20	P	10	H ₃ PO ₄

- The additive or catalyst solutions were made per the following procedures. A phosphorus concentration target of 3.5 wt. % was used for the phosphorus solution.
- 5 Phosphoric acid (13.03 g of 85 %, Food Grade, FMC) was weighed into a tared glass bottle. Ethylene glycol was added until the total solution weight was 100.00 g. A magnetic stir bar was added, and the mixture was stirred.

- A solution of antimony oxide in ethylene glycol was made with a target
- 10 antimony concentration of 1.2 wt. %. Antimony oxide (7.37 g, Fisher) was added into a tared, three-necked, 1-L round-bottomed flask. Ethylene glycol was added until the total solution weight was 500.00 g. The flask was fitted with a heating mantle, condenser, a stopper and a paddle stirrer. The condenser was connected to a nitrogen source and vented through a bubbler to keep air from entering the system. An
 - 15 insulating jacket was placed on the exposed upper portion of the flask. The flask was

heated with stirring until the EG was refluxing vigorously. The mixture was held at reflux for at least 3 hours. The mixture was cooled and filtered through a 0.22 micron cellulose acetate, supported plain filter by Micron Separations, Inc.

5 Oligomers made with a given additive or catalyst were produced in the continuous unit in a block to minimize the magnitude of the transition required. Within a block for a given additive or catalyst, the target levels were randomized. In the interest of minimizing transitions, the highest target level was not run at the beginning of a block. The unit was run for twenty-four hours to make each oligomer.
10 Product was collected in a nitrogen-purged, covered, steel beaker, surrounded by dry ice. The beaker was changed about every three hours. The materials from the last three beakers – representing the last 9 hours of a run – were ground and analyzed. Before polymerization, the beakers judged to be comparable were combined in a large bag with shaking.

15 The carboxyl end groups were determined by titration with base. Additive and catalyst levels were measured by X-ray fluorescence (XRF). Degree of polymerization and mole % reacted CHDM were obtained by NMR spectroscopy of a phenol and 1,1,2,2-tetrachloroethane solution. Percent conversion calculations combined carboxyl
20 end groups and NMR data. After samples were hydrolyzed and silylated, the weight percent of diethylene glycol was measured via a gas chromatography method. Molecular weights were determined by gel permeation chromatography.

Example 1: Esterification in the Presence of a Target of 150 ppm Antimony

25 The slurry put in the feed tank consisted of 3270 g of Amoco TPA, 1585 g of EG, 42.6 g of CHDM, and 46.3 g of antimony solution (x-ray fluorescence measurement: 0.0124 g antimony/g solution). Analyses on the esterification product (Sample 18) resulted in the following data: carboxyl end groups of 370 meq KOH/kg, a percent conversion of carboxyl end groups to ester end groups of 96.3%, a degree of
30 polymerization of 5.6, an antimony level of 135 ppm, a diethylene glycol (DEG) level

of 1.46 wt. %, a reacted CHDM level of 1.43 mole %, a number-averaged molecular weight of 913 g/mole, and a weight-averaged molecular weight of 1621 g/mole.

Example 2: Esterification in the Presence of a Target of 250 ppm Antimony

5 The slurry put in the feed tank consisted of 3270 g of Amoco TPA, 1556 g of EG, 42.6 g of CHDM, and 76.5 g of antimony solution (x-ray fluorescence measurement: 0.0125 g antimony/g solution). Analyses on the esterification product (Sample 9) resulted in the following data: carboxyl end groups of 378 meq KOH/kg, a percent conversion of carboxyl end groups to ester end groups of 96.2%, a degree of
10 polymerization of 5.5, an antimony level of 232 ppm, a diethylene glycol (DEG) level of 1.48 wt. %, a reacted CHDM level of 1.43 mole %, a number-averaged molecular weight of 875 g/mole, and a weight-averaged molecular weight of 1640 g/mole.

Example 3: Esterification in the Presence of a Target of 10 ppm Phosphorus

15 The slurry put in the feed tank consisted of 3270 g of Amoco TPA, 1630 g of EG, 42.6 g of CHDM, and 1.06 g of phosphoric acid solution (x-ray fluorescence measurement: 0.0360 g phosphorus/g solution). Analyses on the esterification product (Sample 20) resulted in the following data: carboxyl end groups of 343 meq KOH/kg, a percent conversion of carboxyl end groups to ester end groups of 96.5%, a degree of
20 polymerization of 5.3, a phosphorus level of 7 ppm, a diethylene glycol (DEG) level of 1.64 wt. %, a reacted CHDM level of 1.33 mole %, a number-averaged molecular weight of 900 g/mole, and a weight-averaged molecular weight of 1606 g/mole.

Example 4: Esterification in the Presence of a Target of 62 ppm Phosphorus

25 The slurry put in the feed tank consisted of 3270 g of Amoco TPA, 1625 g of EG, 42.6 g of CHDM, and 6.57 g of phosphoric acid solution (x-ray fluorescence measurement: 0.0361 g phosphorus/g solution). Analyses on the esterification product (Sample 6) resulted in the following data: carboxyl end groups of 365 meq KOH/kg, a percent conversion of carboxyl end groups to ester end groups of 96.3%, a degree of
30 polymerization of 5.7, a phosphorus level of 48 ppm, a diethylene glycol (DEG) level

of 1.95 wt. %, a reacted CHDM level of 1.30 mole %, a number-averaged molecular weight of 899 g/mole, and a weight-averaged molecular weight of 1660 g/mole.

Per examples 3 and 4, as the phosphoric acid level increased, there was an
5 increase in the DEG level of the esterification product. This trend is illustrated in
Figure 1, which depicts DEG level versus phosphorus level.

B. Polymerization Procedure

10 The melt-phase polymerization stage of the designed experiment was run in
random order. Esterification products were prepared per the preceding section.
Ground esterification product (206 g) was weighed into a one-liter, single-necked,
round-bottomed flask. A 316L stainless steel paddle stirrer and a glass polymer head
were attached to the flask. After attaching the polymer head to a side arm and a purge
15 hose, two nitrogen purges were completed.

The polymerization reactor was operated under the control of a CAMILE™
automation system. After a molten bath of Belmont metal was raised to surround the
flask, the CAMILE™ array was initiated. See the following table for the
polymerization conditions.

20 In a CAMILE™ array, a ramp is defined as a linear change of vacuum,
temperature or stir speed during the specified stage time. After the melting stage (# 2)
ended, a 5-minute catalyst addition stage (# 3) began, and the appropriate additive or
catalyst solution was added within the last minute of this stage. The additive and
catalyst solutions were prepared as described in the Esterification Procedure section.
25 The stirring system was automatically calibrated after stage four and prior to stage
five. The finisher stage (#13) was terminated when the power reached 4.75% three
times. Polymers were cooled to ambient temperature.

CAMILE Polymerization Array

Stage Number	Stage Time (min.)	Temp. (°C)	Vacuum (torr)	Stir Speed (rpm)
1	0.0	265	760	0
2	15	265	760	150 *
3	5.0	265	760	200 *
4	10	265	15 *	200
5	1.0	265	15	100 *
6	47	275 *	15	100
7	1.0	275	15	50*
8	40	275	15	50
9	5.0	275	1.5 *	50
10	5.0	275	0.5 *	50
11	5.0	275	0.5	50
12	1.0	275	1.5 *	50
13	Variable	275	1.5	50

* = Ramp

- 5 The polymers were chopped and ground to pass a 3 mm screen. Ground polymers were shaken on a 40-mesh sieve fitted with a lid and pan. The lid and the pan were removed. A second 40-mesh sieve was placed on top of the first. Compressed air was blown through the pair of sieves. This dust removal process reduced the number of fines that adhered to larger particles during the sieving process.
- 10 The fines would solid-phase polymerize quickly and adversely affect comparisons. The +40 mesh portion of each polymer was shaken through a series of sieves: 10, 12, 14, 16, 18 and 20 mesh. The polymer fraction on each sieve was weighed. To conserve the +12 to +20 mesh portion of each polymer to be used in solid stating, - 20/+40 mesh portion of each polymer was used for precursor testing, except for color.

15

For each sieved polymer, the weights on each sieve (except the 10 mesh) were compared. For each sieve size, the smallest weight among the samples was noted. Combining the smallest weight available for each sieve size, a weight distribution common to all the samples was defined. By minimizing particle size differences among the preparative samples, the standard blend enabled more internally consistent solid-stating rate studies. This standard blend had a total weight of 80.5 g where 8.4 grams were -10/+12 mesh, 32.54 grams were -12/+14 mesh, 20.27 grams were -14/+16 mesh, 14.48 grams were -16/+18 mesh, and 4.81 grams were -18/+20 mesh grinds. Color was measured on the precursor blend.

The inherent viscosity (IV) was measured at 25 deg. C by dissolving 0.50 grams of polymer in 100 mL of 60% phenol and 40% 1,1,2,2-tetrachloroethane by weight. Additive and catalyst levels were measured by X-ray fluorescence (XRF). The carboxyl end groups were determined by titration with base. Color was measured using a HunterLab Color test, which was reported in CIELAB units. The diethylene glycol (DEG) level was measured by dissolving 22 to 28 mg of polymer in a solvent mixture consisting of 70% chloroform-d and 30% trifluoroacetic acid-d and obtaining the NMR spectrum on a 500 MHz instrument.

Example 5: Polymerization of Esterification Product #18 (135 ppm Sb) with Prepolymer Addition of 7 ppm of Phosphorus

Ground esterification product (Sample 18, 206 g) was weighed into a one-liter, single-necked, round-bottom flask. Phosphoric acid (0.03 mL of 3.60 wt./wt. % P solution) was added within the last minute of stage 3. The finisher time (length of stage 13) was 93 minutes. Analyses on the polymer resulted in the following data: IV of 0.552 dL/g, an antimony level of 117 ppm, a phosphorus level of 8 ppm, carboxyl end groups of 14.0 meq/kg, a L* color of 89.3, an a* color of -1.1, a b* color of 4.5, and a DEG level of 1.70 wt.%.

Example 6: Polymerization of Esterification Product #18 (135 ppm Sb) with
Prepolymer Addition of 49 ppm of Phosphorus

Ground esterification product (Sample 18, 206 g) was weighed into a one-liter, single-necked round-bottom flask. Phosphoric acid (0.27 mL of 3.60 wt./wt. % P solution) was added within the last minute of stage 3. The finisher time (length of stage 13) was 224 minutes (3-7 hrs). Analyses on the polymer resulted in the following data: IV of 0.564 dL/g, an antimony level of 140 ppm, a phosphorus level of 48 ppm, carboxyl end groups of 14.1 meq/kg, a L* color of 89.7, an a* color of -1.0, a b* color of 5.2, and a DEG level of 1.73 wt.%.

10

Example 7: Polymerization of Esterification Product #9 (232 ppm Sb) with
Prepolymer Addition of 7 ppm of Phosphorus

Ground esterification product (Sample 9, 206 g) was weighed into a one-liter, single-necked round-bottom flask. Phosphoric acid (0.03 mL of 3.60 wt./wt. % P solution) was added within the last minute of stage 3. The finisher time (length of stage 13) was 60 minutes. Analyses on the polymer resulted in the following data: IV of 0.551 dL/g, an antimony level of 211 ppm, a phosphorus level of 7 ppm, carboxyl end groups of 11.0 meg/kg, a L* color of 89.3, an a* color of -1.3, a b* color of 4.7, and a DEG level of 1.70 wt.%.

20

Example 8: Polymerization of Esterification Product #9 (232 ppm Sb) with
Prepolymer Addition of 49 ppm of Phosphorus

Ground esterification product (Sample 9, 206 g) was weighed into a one-liter, single-necked round-bottom flask. Phosphoric acid (0.27 mL of 3.60 wt./wt. % P solution) was added within the last minute of stage 3. The finisher time (length of stage 13) was 124 minutes. Analyses on the polymer resulted in the following data: IV of 0.566 dL/g, an antimony level of 233 ppm, a phosphorus level of 50 ppm, carboxyl end groups of 12.9 meg/kg, a L* color of 89.7, an a* color of -1.0, a b* color of 4.1, and a DEG level of 1.70 wt.%.

30

Example 9: Polymerization of Esterification Product #20 (7 ppm P) with Prepolymer Addition of 135 ppm of Antimony

Ground esterification product (Sample 20, 206 g) was weighed into a one-liter, single-necked round-bottom flask. Antimony glycolate (2.3 mL of 1.11 wt./wt. % Sb solution) was added within the last minute of stage 3. The finisher time (length of stage 13) was 104 minutes. Analyses on the polymer resulted in the following data: IV of 0.557 dL/g, an antimony level of 122 ppm, a phosphorus level of 8 ppm, carboxyl end groups of 10.9 meg/kg, a L* color of 89.8, an a* color of -1.3, a b* color of 5.5, and a DEG level of 1.82 wt.%.

Example 10: Polymerization of Esterification Product #6 (48 ppm P) with Prepolymer Addition of 135 ppm of Antimony

Ground esterification product (Sample 6, 206 g) was weighed into a one-liter, single-necked round-bottom flask. Antimony glycolate (2.3 mL of 1.11 wt./wt. % Sb solution) was added within the last minute of stage 3. The finisher time (length of stage 13) was 119 minutes. Analyses on the polymer resulted in the following data: IV of 0.567 dL/g, an antimony level of 123 ppm, a phosphorus level of 43 ppm, carboxyl end groups of 14.2 meg/kg, a L* color of 89.3, an a* color of -0.9, a b* color of 5.1, and a DEG level of 2.23 wt.%.

Example 11: Polymerization of Esterification Product #20 (7 ppm P) with Prepolymer Addition of 232 ppm of Antimony

Ground esterification product (Sample 20, 206 g) was weighed into a one-liter, single-necked round-bottom flask. Antimony glycolate (4.3 mL of 1.11 wt./wt. %Sb solution) was added within the last minute of stage 3. The finisher time (length of stage 13) was 76 minutes. Analyses on the polymer resulted in the following data: IV of 0.567 dL/g, an antimony level of 231 ppm, a phosphorus level of 9 ppm, carboxyl end groups of 9.9 meq/kg, a L* color of 89.4, and a * color of -1.3, a b* color of 5.2, and a DEG level of 1.80 wt.%.

Example 12: Polymerization of Esterification Product #6 (48 ppm P) with Prepolymer Addition of 232 ppm of Antimony

Ground esterification product (Sample 6, 206 g) was weighed into a one-liter, single-necked round-bottom flask. Antimony glycolate (4.0 mL of 1.19 wt./wt. % Sb solution) was added within the last minute of stage 3. The finisher time (length of stage 13) was 88 minutes. Analyses on the polymer resulted in the following data: IV of 0.543 dL/g, an antimony level of 214 ppm, a phosphorus level of 39 ppm, carboxyl end groups of 10.5 meq/kg, a L* color of 87.9, an a* color of -0.7, a b* color of 5.3, and a DEG level of 2.20 wt. %.

10

Per examples 5-8, when phosphoric acid was added to esterification product containing antimony (antimony early & phosphoric acid late), the finisher time increased significantly with increasing phosphorus level, especially at the lower antimony level. In contrast, examples 9-12 illustrated that when antimony was added to esterification product containing phosphorus from phosphoric acid i.e., (phosphoric acid early & antimony late), the finisher time was relatively insensitive to phosphorus level. As the additive level increases, the melt-phase production rate of this process will be faster than that of a process adding antimony early and phosphoric acid late. The observed finisher times, the phosphorus addition points, and the measured values of both antimony and phosphorus were used to generate a response surface model with JMP TM statistical software. From the response surface model, the contour plots shown in *Figures 2 & 3* were generated. The numbers on these figures correspond to finisher time in minutes. *Figure 2* illustrates the effect on finisher time of changing phosphorus levels and antimony levels when phosphoric acid is added just prior to the prepolymer stage. *Figure 3* illustrates the effect on finisher time of changing phosphorus levels and antimony levels when phosphoric acid is added up front to the TPA/EG/CHDM paste prior to the esterification stage.

20

25

Per examples 9-12, when phosphoric acid was added before the esterification stage, the diethylene glycol level in the polyester was sensitive to the level of additive

30

present. Therefore, the maximum level of phosphoric acid used can be determined by the maximum level of diethylene glycol (DEG) that could be tolerated.

C. Solid-phase Polymerization

5

Two metal solid-staters were used to solid-phase polymerize the precursors. A CAMILE™ system controlled conditions in the solid-staters – except for nitrogen flow rate, which was controlled manually with a rotameter. Heated nitrogen passed through a frit that supported a bed of precursor. The set point for the nitrogen
10 temperature just below the frit was 205 °C, and the nitrogen flow rate was 14 standard cubic feet per hour. Solid-stating rate studies were done in a random order different than that used for the melt-phase polymerizations. Prior to each solid-stating rate study, the standard particle size blend was thoroughly mixed, and then a 30-gram portion of the blend was removed and poured into a metal solid-stater. The bed was
15 made level.

A sample of approximately 0.6 grams was removed every 30 minutes for six hours. Before each sample was taken, the bed was stirred for 30 seconds using a wire whisk attached to a rod. The stirring mixed the sample bed horizontally and vertically
20 to minimize the effect on IV of particle location in the bed. After a sample of about 0.6 grams was removed, the bed was leveled.

After each rate study was complete, about 22 grams of polymer remained in the solid-stater; this material was isolated and analyzed. These samples had inherent
25 viscosities, which ranged from 0.75 to 0.77 dL/g.

As each rate study was completed, samples were submitted for IV analysis. From the IV data, the solid-phase polymerization time to reach the product IV (0.68 dL/g) for each precursor was determined from a plot of IV as a function of time. For
30 each precursor, the solid-stating time to 0.68 IV determined the length of the preparative solid-stating runs.

Preparative solid-stating runs were performed at the same nitrogen temperature and flow rate used during the rate studies. A random run order was generated for the preparative solid-phase polymerizations. For each precursor, fifty grams of the standard particle size blend were used for the solid-phase preparative run. Although no samples were taken, the bed was stirred and leveled every 30 minutes. The preparative samples were submitted for the following tests: IV, color, acetaldehyde generation, and solution haze.

The acetaldehyde generation test was performed at 295°C. Ten grams of polymer were dried at 120°C overnight. The polymer was placed in a melt indexer for 5 minutes at 295°C, extruded and quenched. The polymer was cryogenically ground and sieved (≤ 20 mesh particle size). An inert gas was passed across the sample (0.50 ± 0.05 grams) at 150 °C for 10 minutes. The gas was then sent to a trap cooled with liquid nitrogen. The trap was then heated to 300°C, and the acetaldehyde was swept into a gas chromatograph for measurement.

The solution haze was measured by dissolving the polymer (10.0 g) in a mixture of methylene chloride and hexafluoro isopropyl alcohol (130 mL, 70:30 v/v). The turbidity of the solution was measured with a Hach Ratio Nephelometric Turbidimeter. The mixtures were centrifuged to isolate the particulates when the solution haze values were ≥ 5 ntu, except for Examples 13 and 15. The particulates were analyzed by x-ray diffraction (XRD) to identify crystalline species and by energy dispersive spectroscopy (EDS) to identify the elements, present, including those in amorphous species.

Example 13: Solid Stating of Polymer with 117 ppm of Antimony and 8 ppm of Phosphorus (Antimony Early/Phosphoric Acid Late)

Polymer was solid stated for 1 hour and 48 minutes. Analyses on the polymer resulted in the following data: IV of 0.665 dL/g, a L* color of 88.8, an a* color of -1.0, a b* color of 4.6, an acetaldehyde generation at 295°C of 12.5 ppm, and a solution haze

value of 4.5 ntu. Per XRD, the particulates contained antimony oxide. EDS indicated that antimony (silicon, copper, iron) was present in the particulates.

5 Example 14: Solid Stating of Polymer with 140 ppm of Antimony and 48 ppm of Phosphorus (Antimony Early/Phosphoric Acid Late)

Polymer was solid stated for 3 hour and 10 minutes. Analyses on the polymer resulted in the following data: IV of 0.673 dL/g, a L* color of 88.9, an a* color of -1.0, a b* color of 5.2, an acetaldehyde generation at 295°C of 11.5 ppm, and a solution haze value of 4.4 ntu.

10

Example 15: Solid Stating of Polymer with 211 ppm of Antimony and 7 ppm of Phosphorus (Antimony Early/Phosphoric Acid Late)

Polymer was solid stated for 1 hour and 51 minutes. Analyses on the polymer resulted in the following data: IV of 0.662 dL/g, an acetaldehyde generation at 295°C of 15.1
15 ppm, and a solution haze value of 4.7 ntu. Per XRD, the particulates contained antimony oxide. EDS indicated that antimony was present in the particulates.

Example 16: Solid Stating of Polymer with 223 ppm of Antimony and 50 ppm of Phosphorus (Antimony Early/Phosphoric Acid Late)

20 Polymer was solid stated for 2 hours and 36 minutes. Analyses on the polymer resulted in the following data: IV of 0.686 dL/g, a L* color of 89.2, an a* color of -1.0, a b* color of 3.9, an acetaldehyde generation at 295°C of 12.2 ppm, and a solution haze value of 6.8 ntu. Per XRD, the particulates contained antimony oxide and antimony phosphate. EDS indicated that antimony and phosphates were present
25 in the particulates.

Example 17: Solid Stating of Polymer with 8 ppm of Phosphorus and 122 ppm of Antimony (Antimony Late/Phosphoric Acid Early)

30 Polymer was solid stated for 2 hours and 7 minutes. Analyses on the polymer resulted in the following data: IV of 0.673 dL/g, a L* color of 89.0, an a* color of -1.2, a b*

color of 5.4, an acetaldehyde generation at 295°C of 11.9 ppm, and a solution haze value of 4 ntu.

Example 18: Solid Stating of Polymer with 9 ppm of Phosphorus and 231 ppm of

5 Antimony (Antimony Late/Phosphoric Acid Early)

Polymer was solid stated for 1 hour and 45 minutes. Analyses on the polymer resulted in the following data: IV of 0.684 dL/g, a L* color of 88.3, an a* color of -1.4, a b* color of 5.4, an acetaldehyde generation at 295°C of 11.7 ppm, and a solution haze value of 5 ntu. Per XRD, the particulates contained antimony oxide. EDS indicated
10 that antimony was present in the particulates.

Example 19: Solid Stating of Polymer with 43 ppm of Phosphorus and 123 ppm of

Antimony (Antimony Late/Phosphoric Acid Early)

Polymer was solid stated for 1 hour and 47 minutes. Analyses on the polymer resulted
15 in the following data: IV of 0.673 dL/g, a L* color of 88.6, an a* color of -0.9, a b* color of 5.5, an acetaldehyde generation at 295°C of 14.0 ppm, and a solution haze value of 3.1 ntu.

Example 20: Solid Stating of Polymer with 39 ppm of Antimony and 214 ppm of

20 Phosphorus (Antimony Late/Phosphoric Acid Early)

Polymer was solid stated for 1 hour and 34 minutes. Analyses on the polymer resulted in the following data: IV of 0.678 dL/g, a L* color of 88.1, an a* color of -0.83, a b* color of 5.2, an acetaldehyde generation at 295°C of 14.1 ppm, and a solution haze value of 3.9 ntu.

25

Per Example 16, when phosphoric acid was added to an esterification product containing antimony, antimony phosphate and antimony oxide were found in the particulates isolated from the solution haze sample. Antimony phosphate can cause haze in polyesters. Per Example 18, when antimony was added to an esterification
30 product containing phosphorus from phosphoric acid, only antimony oxide was found in the particulates isolated from the solution haze sample. Potential haze problems

due to antimony phosphate formation were precluded by adding phosphoric acid early and antimony late.

Example 21: A Phosphate Triester as the Phosphorus Source

5 When a phosphate triester like tri-t-butyl phosphate is the phosphorus source, the trends are different than those observed for phosphoric acid. When the antimony is added early and the phosphate triester is added late, the melt-phase finisher time is relatively insensitive to the phosphorus level. The dramatic increase in finisher time with increasing phosphorus level for early antimony/late phosphoric acid addition is
10 not seen when the phosphorus source is a phosphate triester. When the antimony is added early and the phosphate triester is added late, antimony oxide alone is found in the particulates isolated from solution haze samples. In contrast to the situation with late addition of phosphoric acid, particulate haze from antimony phosphate is not a concern when a phosphate triester is added late.

15

When the phosphate triester is added early and the antimony is added late, the melt-phase finisher time increases with increasing phosphorus level. The stability in finisher time with increasing phosphorus level for early phosphoric acid/late antimony addition is not seen when the phosphorus source is a phosphate triester.

20

While the invention has been described in terms of various preferred embodiments thereof, it should be understood that various modifications, changes, substitutions, omissions and the like may be made without departing from the spirit of the invention. Thus, the scope of the invention is limited only by the scope of the
25 following claims including equivalents thereof.

CLAIMS**What is claimed is:**

1. A process for making polyester resin comprising
 - (a) esterifying at least one dicarboxylic acid component and at least one diol component; and
 - (b) polymerizing the product of step (a) under conditions effective to provide a polyester resin,wherein:
 - (1) polymerization step (b) occurs in the presence of (i) an antimony-based polymerization catalyst and (ii) an acidic phosphorus-containing additive, with the catalyst (i) being added after the additive (ii), and
 - (2) the acidic phosphorus containing additive (ii) is added sufficiently before the polycondensation catalyst (i) such that the additive (ii) can react with the at least one diol.
2. A process for making polyester resin comprising
 - (a) esterifying at least one dicarboxylic acid component and at least one diol component; and
 - (b) polymerizing the product of step (a) under conditions effective to provide a polyester resin,wherein:
 - (1) polymerization step (b) occurs in the presence of (i) an antimony-based polymerization catalyst and (ii) an acidic phosphorus-containing additive, with the catalyst (i) being added after the additive (ii), and

- (2) the acidic phosphorus containing additive (ii) is selected such that the reaction rate of the polymerization step (b) is relatively insensitive to the level of additive (ii).
3. The process according to claim 2, wherein the length of time between the addition of the additive and the catalyst is sufficient to allow a reaction between the additive and the diol.
 4. The process according to claim 1, wherein the additive (ii) is added prior to a point in the step (a) where the at least one diol will have a partial pressure such that the at least one diol will boil away.
 5. The process according to claim 4 wherein the partial pressure of the diol compound is not less than about 300 Torr.
 6. The process according to claim 1, further comprising:
(a) solid-phase polymerization of the polyester resin from step (b).
 7. The process according to claim 1, further comprising a prepolymer reaction stage between the esterification step (a) and polymerization reaction (b).
 8. The process according to claim 7, wherein the additive (ii) is added immediately prior to, or during the prepolymer stage.
 9. The process according to claim 7 wherein the catalyst (i) is added immediately prior to, during, or after the prepolymer stage, but prior to the polymerization step.
 10. The process according to claim 1, wherein the additive (ii) is added immediately prior to, or during the esterification step (a).

11. The process according to claim 5, wherein the polyester resin is a poly(ethylene terephthalate) (PET) resin or a modified PET resin.
12. The process according to claim 1, wherein the at least one dicarboxylic acid comprises terephthalic acid.
13. The process according to claim 12 wherein the terephthalic acid is present in an amount of from about 80 mole % to about 95 mole %.
14. The process according to claim 1, wherein the at least one diol component comprises a glycol having from about 2 to about 10 carbon atoms.
15. The process according to claim 1, wherein the at least one diol component comprises ethylene glycol.
16. The process according to claim 15 wherein the ethylene glycol is present in an amount of from about 80 mole % to about 95 mole %.
17. The process according to claim 1, wherein the polyester resin is modified with at least one additional diacid component is selected from aromatic dicarboxylic acids having 8 to 14 carbon atoms, aliphatic dicarboxylic acids having 4 to 12 carbon atoms, cycloaliphatic dicarboxylic acids having 8 to 12 carbon atoms and mixtures thereof, wherein the additional diacid component(s) are present in the amount of about 1 mole % to 20 mole %.
18. The process according to claim 17, wherein the at least one additional dicarboxylic acid component is phthalic acid, isophthalic acid, 2,6-naphthalenedicarboxylic acid, 1,4-cyclohexanedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, diphenyl-4,4'-dicarboxylic acid, stilbenedicarboxylic acid, succinic acid, glutaric acid, adipic acid, sebacic acid, cyclohexane diacetic acid, azelacetic acid or 1,12-dodecanedioic acid.

19. The process according to claim 1 wherein the polyester resin is modified with at least one additional diol component selected from cycloaliphatic diols having 6 to 20 carbon atoms, aliphatic diols having 3 to 20 carbon atoms, and mixtures thereof, wherein the additional diol component(s) are present in the amount of about 1 mole % to 20 mole %.
20. The process according to claim 19, wherein the at least one additional diol component is 1,4-cyclohexanedimethanol (CHDM), diethylene glycol, triethylene glycol, 1,2-propanediol, 1,3-propanediol, neopentyl glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,2-cyclohexanediol, 1,4-cyclohexanediol, 1,2-cyclohexanedimethanol, 1,3-cyclohexanedimethanol, 3-methylpentanediol-(2,4), 2-methylpentanediol-(1,4), 2,2,4-trimethylpentanediol-(1,3), 2-ethylhexanediol-(1,3), 2,2-diethylpropane-diol-(1,3), hexanediol-(1,3), 1,4-di-(hydroxyethoxy)-benzene, 2,2-bis-(4-hydroxycyclohexyl)-propane, 2,4-dihydroxy-1,1,3,3-tetramethyl-cyclobutane, 2,2-bis-(3-hydroxyethoxyphenyl)-propane, 2,2-bis-(4-hydroxypropoxyphenyl)-propane, 1,2-cyclohexanediol, 1,4-cyclohexanediol or mixtures thereof.
21. The process according to claim 1, wherein the polymerization step (b) is a polycondensation reaction and the catalyst (i) is a polycondensation catalyst.
22. The process according to claim 1 wherein the antimony-based catalyst (i) is a diol-soluble compound of antimony (III) or antimony (V) or a compound of antimony (III) or antimony (V) that becomes soluble upon reaction with the diol.
23. The process according to claim 1, wherein the antimony-based catalyst (i) is selected from the group of antimony (III) oxide, antimony (III) acetate, antimony (III) glycolates, antimony (III) ethyleneglycoxide and mixtures thereof.

24. The process according to claim 1, wherein the antimony-based catalyst (i) is antimony oxide that is present in an amount effective to provide elemental antimony of from about 75 ppm to about 400 ppm in the polymer.
25. The process according to claim 1, wherein the acidic phosphorus-containing additive (ii) comprises phosphoric acid, phosphorous acid, polyphosphoric acid, acidic phosphate esters or mixtures thereof.
26. The process according to claim 1, wherein the acidic phosphorus-containing additive (ii) comprises phosphoric acid.
27. The process according to claim 1, wherein the acidic phosphorus-containing additive (ii) is present in the amount between about 20 and about 45 ppm of elemental phosphorus based on the weight of the polymer.
28. The process according to claim 1, wherein the acidic phosphorus-containing additive (ii) is present in the amount of less than about 15 ppm of elemental phosphorus based on the weight of the polymer.
29. The process according to claim 1 wherein catalyst residue from step (b) is at least substantially free of antimony phosphate compounds.
30. The process according to claim 1, wherein the polyester resin has an intrinsic viscosity of about 0.4 to 1.2 dL/g measured at 25 C by dissolving 250 mg of polyester in 50 mL or a solvent consisting of a 60:40 ratio by weight of phenol and tetrachloroethane.
31. The process according to claim 1, wherein the polymerization step (b) is performed in the absence of added cobalt compound(s).

32. The process according to claim 1, wherein the polymerization step (b) is performed in the presence of at least one organic toner selected from among red organic toners, and blue organic toners.
33. A polyester product produced by the process according to claim 1.
34. A polyester containing (a) elemental phosphorus present in an amount not greater than about 75 ppm and (b) at least one organic toner selected from among organic blue toners and organic red toners, which toner(s) are present in an amount of about 0.5 to about 10 ppm.
35. The polyester according to claim 34 wherein the elemental phosphorus is present in an amount less than about 15 ppm based on elemental phosphorus.
36. The polyester according to claim 34 having at least one organic red toner present in an amount of about 0.5 to about 3 ppm.
37. The polyester according to claim 34 having at least one organic blue toner present in an amount of about 1 to about 7 ppm.

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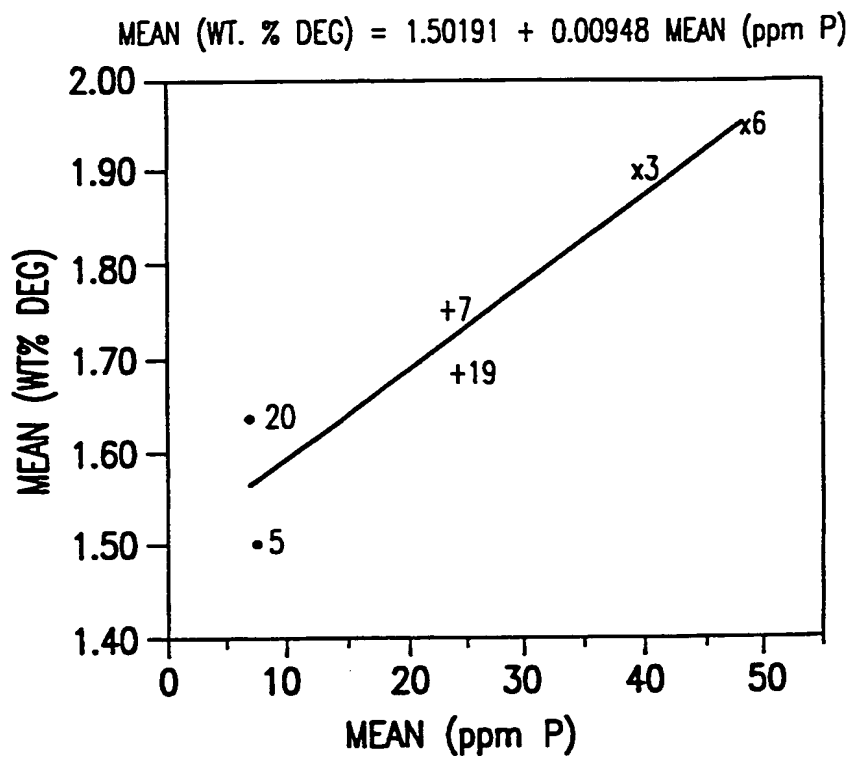


FIG.1

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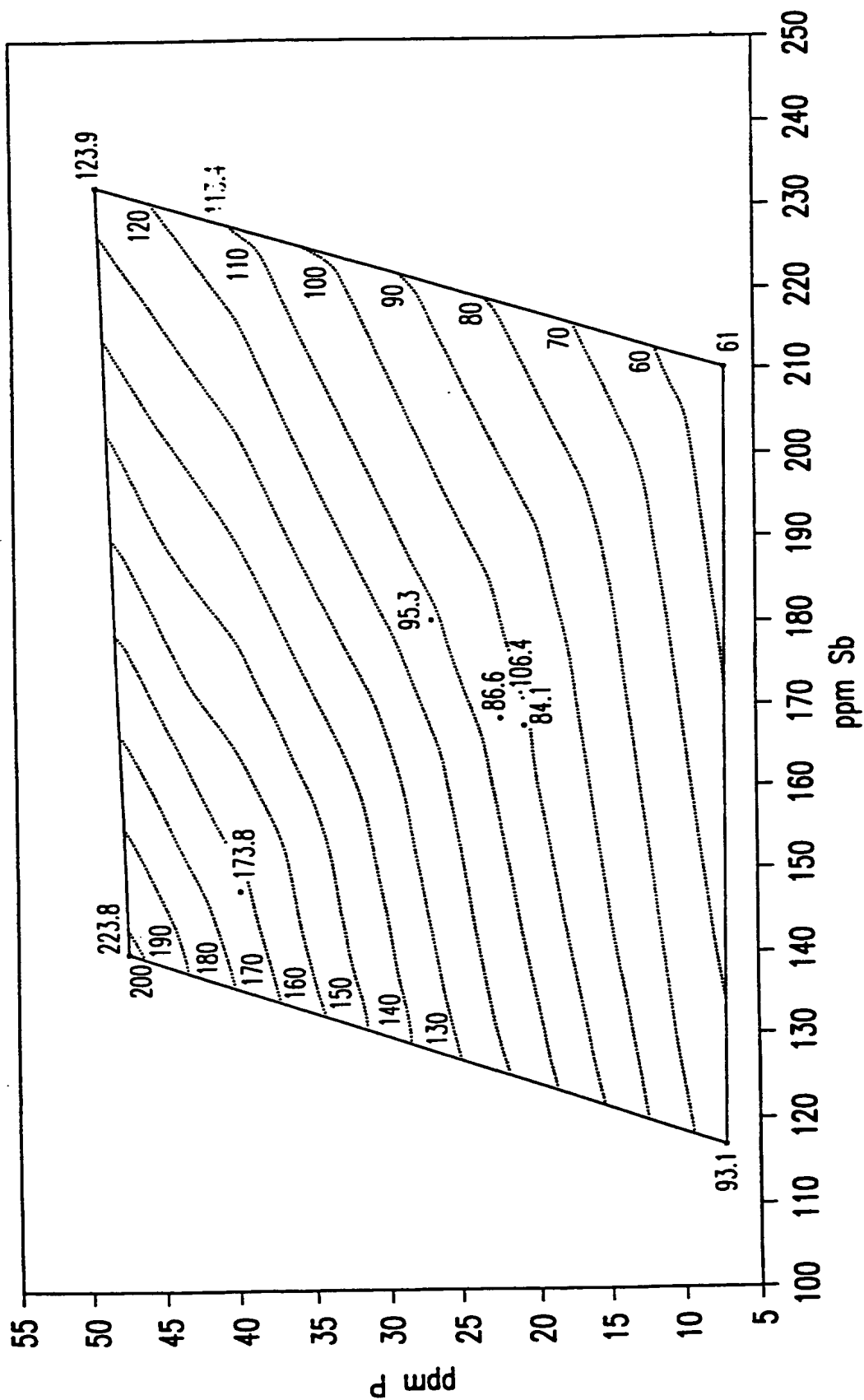


FIG.2

SUBSTITUTE SHEET (RULE 26)

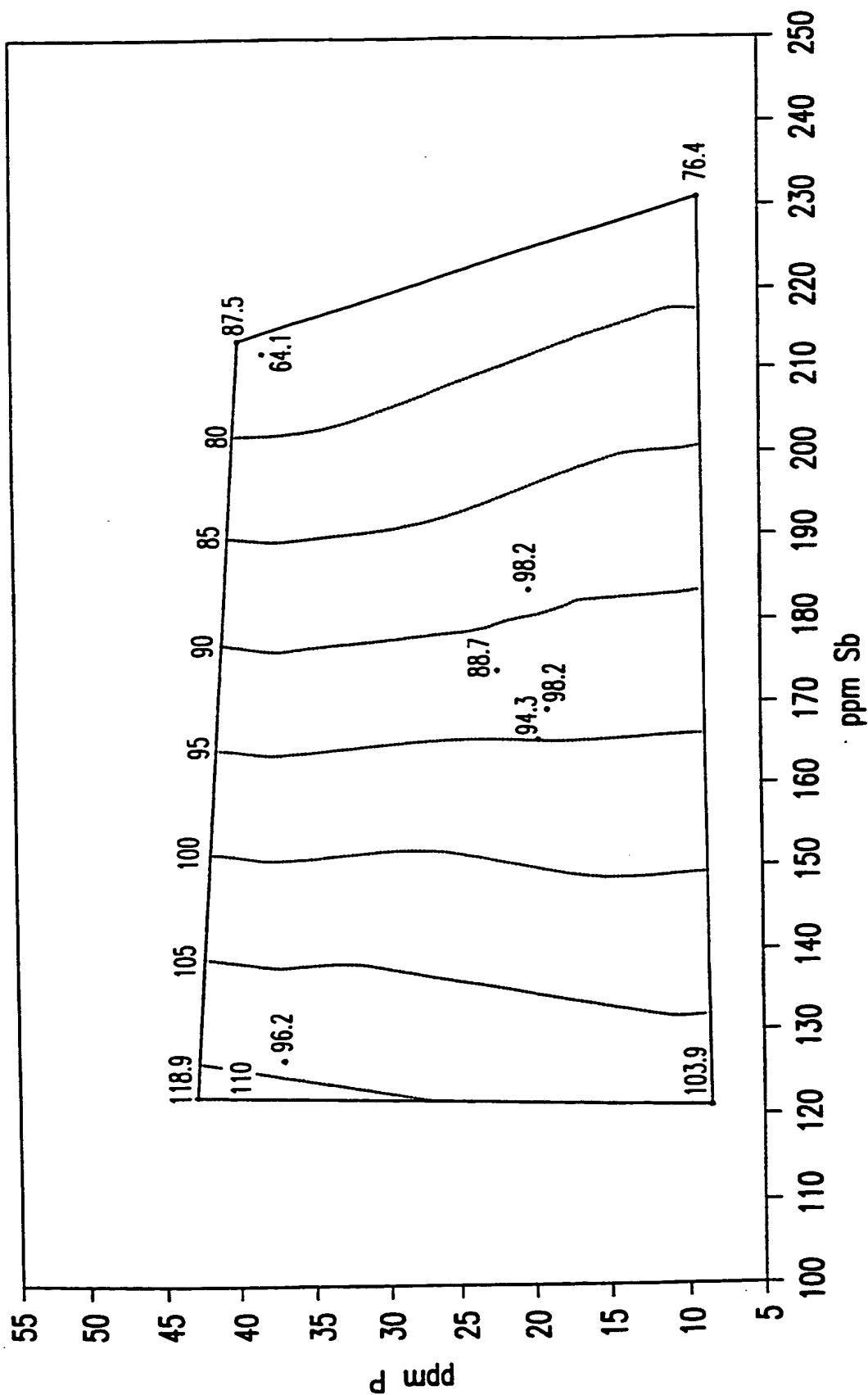


FIG.3

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INTERNATIONAL SEARCH REPORT

national Application No
PCT/US 99/19385

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08G63/86 C08G63/82 C08G63/78

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 061 414 A (GOODYEAR TIRE & RUBBER) 29 September 1982 (1982-09-29)	1-7, 9-12, 14, 15, 21-26, 28, 30, 33
Y	claims 6-9; example; table I page 12, line 13 -page 14, line 11 & US 4 499 226 A cited in the application ----- -/--	13, 17-20, 31, 32

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

20 April 2000

Date of mailing of the international search report

04/05/2000

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Krische, D

INTERNATIONAL SEARCH REPORT

national Application No

PCT/US 99/19385

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	claims 5,6; ex mple 1 & US 5 235 027 A cited in the application	13, 17-20, 31, 32
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I, national Application No

PCT/US 99/19385

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

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